

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 18/08, 18/46, 18/48, 18/40, C08F 290/14, 283/00, C09D 17/00, 7/02, C08J 3/03 // C08L 67:08	A1	(11) International Publication Number: WO 97/19120 (43) International Publication Date: 29 May 1997 (29.05.97)
(21) International Application Number: PCT/EP96/05156 (22) International Filing Date: 21 November 1996 (21.11.96) (30) Priority Data: 95203185.4 21 November 1995 (21.11.95) EP (34) Countries for which the regional or international application was filed: NL et al. (71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): BUTER, Roelof [NL/NL]; Surinkhof 1, NL-6952 HT Dieren (NL). COENJAARTS, Norbert, Johan [NL/NL]; Van Reigersbergenstraat 518, NL-1052 WG Amsterdam (NL). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).		(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: WATER-DISPERSIBLE UNSATURATED POLYURETHANE (57) Abstract <p>A water-dispersible unsaturated polyurethane comprising pendant unsaturated alkyl groups, pendant sulphonic acid salt groups and pendant alkoxy polyoxyalkylene groups is described. The sulphonic acid salt groups and alkoxy polyoxyalkylene groups are present in amounts at least sufficient to render the unsaturated polyurethane water dispersible. The unsaturated polyurethane is especially suited for dispersing alkyds in water. Also disclosed is a composite latex comprising an aqueous alkyd dispersion and monoethylenically unsaturated monomers and a pigment dispersion comprising a pigment or pigment paste and the unsaturated polyurethane.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

WATER-DISPERSIBLE UNSATURATED POLYURETHANE

5 The invention pertains to a water-dispersible unsaturated polyurethane comprising pendant unsaturated alkyl groups, pendant sulphonic acid salt groups, and polyoxyalkylene groups, said sulphonic acid salt groups and said polyoxyalkylene groups being present in amounts at least sufficient to render said unsaturated polyurethane water dispersible.

10

Such an unsaturated polyurethane is known from European patent application EP-A-0 613 914. The unsaturated polyurethane disclosed in that document comprises ionic groups, unsaturated alkyl groups, and polyoxyalkylene groups built into the polyurethane main chain.

15

It has now been found that an unsaturated polyurethane having certain pendant groups permits efficient dispersion, suspension, emulsion, etc. in water of hydrophobic polymers and pigments.

20 The invention is a water-dispersible unsaturated polyurethane of the above-mentioned type characterised in that the polyoxyalkylene groups are pendant alkoxy polyoxyalkylene groups.

In a particular embodiment, the unsaturated polyurethane according to the invention is of the above-disclosed type comprising

- 25 a) 10-40 wt.%, preferably 15-20 wt.%, C1-C4 alkoxy polyoxyalkylene groups,
- b) 0,1-0,5 meq. per gram, preferably 0,2-0,35 meq. per gram, alkali metal salt of sulphonic acid, and
- 30 c) 10-35 wt.%, preferably 20-30 wt.%, unsaturated, preferably polyunsaturated, alkyl groups.

European patent application EP-A-0 309 114 discloses a non-ionic polyurethane resin having pendant polyoxyethylene chains and, optionally, free acid groups. Sulphonic acid groups or salts thereof are not disclosed.

- 5 EP-A-0 013 112 discloses an aqueous emulsion comprising an organic isocyanate and a surfactant. The surfactant is a polyurethane dispersing resin with pendant alkoxy polyoxyethylene groups and an isocyanate reactive compound having, optionally, carboxylic acid groups. Sulphonic acid groups or salts thereof are not mentioned.

10

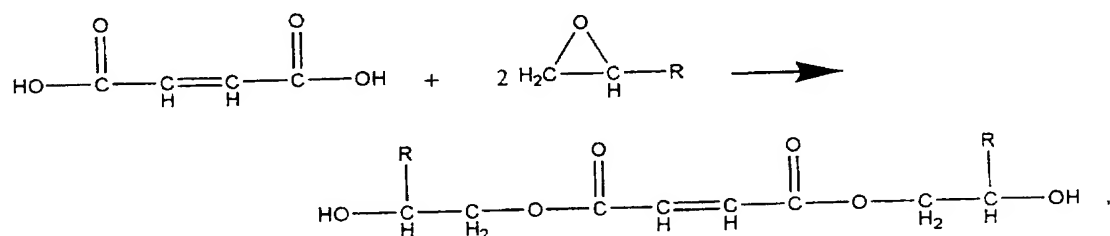
- The sulphonic acid salt groups and the alkoxy polyoxyalkylene groups present in the unsaturated polyurethane of the current invention need to be present in amounts at least sufficient to render the unsaturated polyurethane water dispersible. The necessary amounts will vary according factors such as, for
15 non-limiting example, the specific unsaturated polyurethane, the use to be made of the unsaturated polyurethane, the aqueous system, other compounds present, etc. These amounts are readily determined by a skilled artisan based on, for non-limiting example, the character of the unsaturated polyurethane and the further teachings found herein.

20

- The unsaturated polyurethane of the current invention can be prepared, for example, by reacting diisocyanate with a compound containing alkoxy polyoxyalkylene groups and two isocyanate reactive groups, a compound containing ionic groups and two isocyanate reactive groups, and a compound
25 containing unsaturated alkyl groups and one isocyanate reactive group or a compound which is a reaction product of an unsaturated fatty acid and a mono-epoxide.

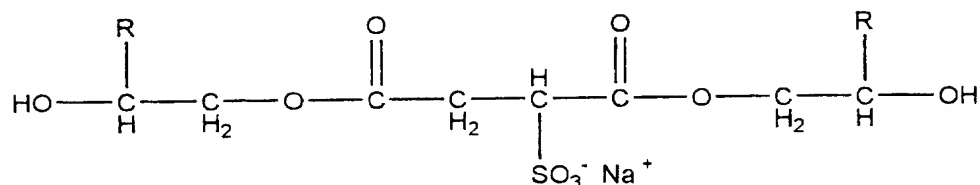
Non-limiting examples of suitable compounds for use in incorporating the C1-C4 alkoxy polyoxyalkylene groups into the unsaturated polyurethane include: methoxy polyethylene glycols, polyether-1,3-propanediols, such as Tegomer[®] D-3123 (PO/EO = 15/85, Mn = 1180), Tegomer[®] D-3409 (PO/EO = 0/100, Mn = 2240), and Tegomer[®] D-3403 (PO/EO = 0/100, Mn = 1180) (Tegomer[®] products available from Goldschmidt AG, Germany). In addition, reaction products of 1 or 2 moles of mono epoxide and polyoxyalkylene amines can be used, e.g., methoxy polyoxyethylene/polyoxypropylene amines, which are available from Huntsman Corporation, Zaventem, Belgium under the trade designation Jeffamine[®], such as Jeffamine[®] M-1000 (PO/EO = 3/19, Mn = 1100) and Jeffamine[®] M-2070 (PO/EO = 10/32, Mn = 2200). It is preferred to employ alkoxy polyoxyalkylene groups having an average molecular weight of 500-3000.

15 Suitable compounds for incorporating the sulphonic acid salt groups into the unsaturated polyurethane include alkali metal-, particularly Na-, K-, and Li-, sulphosuccinates. A non-limiting method of preparing such sulphosuccinates is a two step preparation process wherein 1) fumaric or maleic acid is converted into a diester diol with the aid of a mono-epoxide:

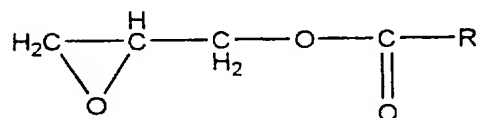


wherein R is selected from hydrogen or a C₁₋₄₀ alkyl group, and 2) the diester diol is reacted with, e.g., NaHSO₃, to provide a compound having the following structure:

25



In addition, reaction products of 1 or 2 moles of mono epoxide and 1 mole of an alkali metal salt, preferably a Na-, K- or Li-salt, of an aminosulphonic acid compound such as amino ethane sulphonic acid (taurine) or HO-functional esters of 5-(Na-sulpho)-isophthalic acid can be used. Suitable mono epoxides for use in the above-mentioned reactions include: propylene oxide, 1,2-epoxy-octane, and the glycidyl ester of a carboxylic acid according to the formula:



10

wherein R is an alkyl group having 4-40 carbon atoms, in particular the glycidyl ester of 1,1-dimethyl heptane carboxylic acid (available as Cardura® E 10 from Shell Chemicals). Another example of a compound suitable for use in incorporating the sulphonic acid salt groups into the unsaturated polyurethane is the reaction product of 1 mole of NaHSO₃ and 1 mole of propoxylated butene-2-diol-1,4 (having about 2 to 6, preferably about 3 to 5 moles of propylene oxide).

Fatty alcohols and fatty amines can be used to incorporate the unsaturated alkyl groups into the unsaturated polyurethane. Preferred are polyunsaturated mono alcohols and mono amines. Non-limiting examples of suitable fatty alcohols are: oleyl alcohol, linoleic alcohol, linolenic alcohol, linoleyl alcohol, and mixtures thereof. Non-limiting examples of fatty amines are oleyl amine,

20

linoleic amine, linolenic amine, linoleyl amine, the commercially available Genamin[®] from Hoechst, and mixtures thereof.

5 The reaction products of an unsaturated fatty acid and a mono epoxide can also be used to incorporate unsaturated alkyl groups into the unsaturated polyurethane according to the current invention. Polyunsaturated fatty acids are preferred. Non-limiting examples of fatty acids which can be used are linseed oil fatty acid, sunflower oil fatty acid, soybean oil fatty acid, and other natural or synthetic unsaturated fatty acids. Preferred mono epoxides are
10 propylene oxide, 1,2-epoxy octane, and mono epoxides of the Cardura[®] E-series from Shell Chemicals.

The unsaturated polyurethane can be made using isocyanate-functional compounds. Examples of isocyanates which can be used are aliphatic,
15 cycloaliphatic or aromatic di-, tri-, or tetraisocyanates which can be ethylenically unsaturated. Especially suitable are diisocyanates. Non-limiting examples of such diisocyanates are toluene diisocyanate, 4,4'-diisocyanato diphenyl methane, 1,6-diisocyanatohexane, tetramethyl xylylene diisocyanate, isophorone diisocyanate (1-isocyanato-3,3,5-trimethyl-5-
20 isocyanatomethylcyclohexane).

If so desired, small amounts of diols can be added as chain extenders when preparing the unsaturated polyurethane, e.g., polyester or polyether diols such as neopentyl glycol adipate or polypropylene glycol having an average Mw of
25 300-3000.

When preparing the unsaturated polyurethane the ratio of the isocyanate groups of the diisocyanate to the hydroxyl groups (and optionally amino groups) derived from the other compounds is typically about 0.9-1.1:1, most

preferably about 1:1. The unsaturated polyurethane can be prepared in one or several steps. For instance, it is possible to first react the polar compounds such as those supplying the alkoxy polyoxyalkylene groups and sulphonic acid salt groups with the isocyanate functional compounds and then complete the
5 reaction with the unsaturated alkyl supplying compounds. Alternatively, all hydroxyl (and optionally amine)-containing compounds are mixed before being reacted with the isocyanate functional compounds. All hydroxyl (and optionally amine)-containing compounds can be premixed in the reactor at elevated temperature, divested of solvents, if any, by distilling off at reduced pressure,
10 and then reacted with the isocyanate functional compounds. The unsaturated polyurethane is preferably prepared in a dry atmosphere at a temperature of 50-140°C, preferably 90-130°C.

If so desired, a catalyst can be employed, e.g., an organometal compound
15 such as dibutyl tin diacetoacetate and -dilaurate, in a conventional amount of 0,01-0,1 wt.%. Preferably, the preparation of the unsaturated polyurethane is carried out in bulk or with a small quantity of organic solvent (5-10 wt.%) which is inert in relation to the isocyanate functional compound. Optionally, after its preparation, the unsaturated polyurethane can be thinned with another organic
20 solvent to a viscosity at which the resin will become processable.

The unsaturated polyurethane of the current invention is particularly useful as an aid to the dispersion of hydrophobic polymers and pigments in water. Non-limiting examples of hydrophobic polymers are polyesters, polyacrylates,
25 polyurethanes, and, in particular, alkyd resins.

The invention further pertains to aqueous alkyd dispersions comprising the unsaturated polyurethane according to the invention, and to the preparation of such dispersions. Aqueous dispersions comprising about 5-25 wt.%

unsaturated polyurethane resin and about 95-75 wt.% alkyd resin are particularly preferred.

5 Preferably, the alkyd resin used has an oil length of about 40-90 and an acid number of about 0,5-15 mg KOH/g, preferably 5-10 mg KOH/g. If so desired, the acid groups of the alkyd resin can be wholly or partially neutralised with a base, preferably an alkali metal base, most preferably NaOH, KOH or LiOH.

10 Aqueous dispersions of alkyd resins, including conventional alkyd resins which generally have an oil length of about 40-90 and an acid number of about 5-10 mg KOH/g, can be emulsified in water with the aid of the unsaturated polyurethane resin, with the acid groups derived from the alkyd resin(s) simultaneously being neutralised wholly or in part with a base such as NaOH, KOH or LiOH. To this end an alkyd resin is mixed with the unsaturated
15 polyurethane in a ratio of about 75-95 wt.%, preferably about 85-95 wt.%, alkyd resin, about 5-25 wt.%, preferably about 5-15 wt.%, unsaturated polyurethane, and a small quantity of Na-, K- or LiOH. The particle size of such dispersions is typically about 50-800 nm, preferably about 100-500 nm.

20 Next, the mixture of alkyd resin, unsaturated polyurethane, and base is heated to a temperature in the range of 100 to 150°C, optionally with (any) solvents present being distilled off under reduced pressure. After the removal of (any) present solvents the mixture is cooled. At a temperature of about 70 to 100°C, preferably of about 80 to 90°C, the addition of water is started, with vigorous
25 stirring, over a period of 2-4 hours, with the temperature of the mixture gradually being lowered to ambient temperature. A stable alkyd dispersion in water is obtained with a viscosity of 0,1-1 Pa.s, preferably 0,2-0,5 Pa.s. The resulting aqueous alkyd dispersions generally have a solids content of about 40 to 70 wt.%, preferably 50-60 wt.%.

In addition to the described inverse emulsification of a mixture of alkyd resin and the unsaturated polyurethane by adding water to the mixture, the mixture can also be dispersed in water directly. In that case a mixture of alkyd resin and unsaturated polyurethane is preferably heated to a temperature in the range of about 60 to about 100°C. This mixture is pumped into a reactor containing water, with vigorous stirring. Optionally, a small quantity of base, preferably NaOH, KOH or LiOH, can be present in the water to neutralise any carboxylic acid groups of the alkyd resin present. If so desired, special equipment can be employed in which a mixture of alkyd resin is dispersed in water with high shearing forces, for instance, a colloid mill.

The invention also pertains to an aqueous polymer dispersion in which about 10-90 wt.%, preferably about 30-70 wt.%, of the solids content is derived from an alkyd dispersion according to the invention and about 90-10 wt.%, preferably about 70-30 wt.%, is derived from an addition polymer obtained by dispersion polymerisation in the presence of an alkyd dispersion according to the invention.

A wide range of monoethylenically unsaturated monomers and mixtures thereof can be employed to prepare such an addition polymer, e.g.: (cyclo)alkyl(meth)acrylates having 1-12 carbon atoms in the (cyclo)alkyl group, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, (iso)butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, isobornyl(meth)acrylate, dodecyl(meth)acrylate, and cyclohexyl(meth)acrylate; monovinyl aromatic compounds, such as styrene, vinyl toluene, α -methylstyrene, and vinyl naphthalene; other substituted (meth)acrylate compounds, such as (meth)acrylamide, (meth)acrylonitrile, N-methylol(meth)acrylamide, and N-alkyl(meth)acrylamides; and other mono-

unsaturated compounds, such as vinyl chloride, vinyl acetate, and vinyl propionate. In addition, small quantities can be used of: (cyclo)alkyl esters of dicarboxylic acids having 1-12 carbon atoms in the (cyclo)alkyl group, such as dimethyl maleate, diethyl maleate, dipropyl maleate, dibutyl maleate, 2-ethylhexyl maleate, octyl maleate, isobornyl maleate, dodecyl maleate, and cyclohexyl maleate, diethyl fumarate, dibutyl fumarate, and 2-ethylhexyl fumarate; (meth)acrylates containing ether groups, such as 2-methoxyethyl(meth)acrylate, 2-ethoxyethyl(meth)acrylate, 3-methoxypropyl(meth)acrylate; hydroxy(meth)acrylates, such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 4-hydroxybutyl(meth)acrylate, 6-hydroxyhexyl(meth)acrylate, p-hydroxycyclohexyl(meth)acrylate and alkoxy derivatives thereof, such as hydroxypolyethyleneglycol (meth)acrylate, and hydroxypolypropyleneglycol (meth)acrylate,.

15

If so desired, anionic or non-ionic emulsifiers can be employed during the emulsion polymerisation. Non-limiting examples of suitable anionic emulsifiers are potassium laurate, potassium stearate, potassium oleate, sodium decyl sulphate, sodium dodecyl sulphate, sodium dodecyl benzene sulphonate, and sodium rosinate. Non-limiting examples of non-ionic emulsifiers are: linear and branched alkyl polyethylene glycol and alkylaryl polyethylene glycol, polypropylene glycol ethers and polypropylene thioethers, alkyl phenoxypoly(ethylenoxy)ethanols such as the adduct of 1 mole of nonylphenol to 5-12 moles of ethylene oxide, or the ammonium salt of the sulphate of this adduct. During the emulsion polymerisation process use can be made of conventional radical initiators in the usual amounts. Examples of suitable radical initiators are ammonium persulphate, sodium persulphate, potassium persulphate, bis(2-ethylhexyl)peroxydicarbonate, di-n-butyl peroxydicarbonate, t-butyl persulphate, t-butyl hydroperoxide, cumene hydroperoxide, dibenzoyl

25

peroxide, dilauroyl peroxide, 2,2-azobisisobutyronitrile, and 2,2-azobis-2-methyl butyronitrile. Reducing agents suitable for use in combination with, e.g., a hydroperoxide include: ascorbic acid, sodium sulfoxylate, sodium sulfoxylate formaldehyde, thiosulphites, disulphites, hydrosulphites, water-
5 soluble amines, such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, N,N-dimethyl ethanolamine, N,N-diethyl ethanolamine, and reducing salts, such as cobalt sulphate, iron sulphate, nickel sulphate, and copper sulphate. If so desired, a chain regulating agent can be employed, e.g., n-octyl mercaptan, dodecyl mercaptan, and 3-
10 mercaptopropionic acid.

The dispersed polymer particles can be composed of a physical mixture of an addition polymer, such as a polyacrylate, and an alkyd. However, if graft polymerisation occurs during the emulsion polymerisation process, the alkyd
15 resin can be partially combined with the addition polymer, giving dispersed polymer particles composed in part of block polymers and graft polymers of alkyd and addition polymers.

The thus produced composite latex has a solids content of about 30 to 55
20 wt.%, preferably of about 35 to 50 wt.%.

The aqueous alkyd dispersions and polymer dispersions according to the invention are preferably used to formulate coating compositions. When used as such, the dispersions can contain a wide range of other additives common
25 in the coatings industry, such as pigments, extenders, dispersing agents, thixotropy and rheology control agents, as well as siccatives. The group of siccatives is commonly held to include the metal soaps of alkaline-earth metals and heavy metals of monovalent carboxylic acids such as naphthenic acid, octanoic acid or 2-ethyl hexanoic acid. Primary active siccatives contain Co,

Mn, Fe or Ce; supplementary siccatives can contain Pb, Ca, Zn, Ba or Zr. They are conventionally used in an amount of about 0,01 to 0,5 wt.%, calculated on the solids content of the coating composition. Other suitable siccatives include Co(II)(acetylacetonate)₂ and Zr(IV)(acetylacetonate)₄. If so
5 desired, the siccatives can be co-dispersed with the alkyd and the unsaturated polyurethane.

The coating compositions based on the disclosed alkyd dispersions can include special emulsifiers to obtain a spontaneous emulsion in water.
10 Siccatives which can be emulsified in water are commercially available. An anti-skinning agent can be incorporated into the coating compositions to ensure pot life. Examples of anti-skinning agents are oxims, such as butyraldoxim and ethyl methyl ketoxim. Favourable results are generally obtained when a quantity of about 0,01 to 1 wt.%, calculated on the quantity of
15 film-forming constituents, is employed for each of the siccatives as well as the anti-skinning agent.

The coating compositions according to the invention can be applied onto any known substrate such as wood, synthetic materials, and metals. Suitable
20 application methods include rolling, spraying, sprinkling, dipping, and electrostatic spraying. Of course it is also possible to apply the coating composition by simple brushing.

The coating composition can be dried and cured under a variety of conditions,
25 e.g., at room temperature. Accelerated curing can be accomplished by baking at elevated temperatures in the range of, e.g., about 30 to 80°C typically over a period of 20 to 60 minutes.

The coating compositions according to the invention can be used as a primer or filler and also in clear and coloured paints.

5 The unsaturated polyurethane according to the invention is also highly suitable as a pigment dispersing agent. Such a dispersing agent can be prepared without solvents, or there can be solvent removal through distillation under reduced pressure, followed by dispersion in water. Stable aqueous pigment pastes can be obtained by using preferably about 1-10 wt.% (on solids) of the unsaturated polyurethane in relation to the pigment. Each
10 pigment can be dispersed in water with the unsaturated polyurethane, e.g., TiO_2 , phthalocyanine, iron oxide, etc., or pigments can be mixed and the mixture dispersed.

The invention will be further illustrated with reference to the following non-
15 limiting examples.

Experimental

The following examples disclose the preparation of a number of unsaturated polyurethanes and stable aqueous alkyd dispersions, as well as coating compositions prepared using the unsaturated polyurethane prepared according to the invention. The properties of the dispersions are listed in the tables. The average particle size of the dispersions in the examples was determined by dynamic light scattering, the dispersions being diluted to a solids content of about 0,1 wt.%. The viscosity was determined with a Brookfield viscometer (LV=4; 60 rpm). The solids content was determined in accordance with ASTM method 1644-59, after 30 minutes of heating at 140°C.

As sulphonic acid salt containing compound, a reaction product of 1 mole of maleic acid, 2 moles of Cardura® E 10, and 1 mole of NaHSO₃ (acid number<1, Mw = 720, 70% in 1-methoxypropanol-2) is used in the following examples. The compound is further indicated as "NaHSO₃-compound".

Preparation of Unsaturated Polyurethane A

The following compounds were weighed into a 2 l reaction flask :

194,7 g	Tegomer® D-3123,
344,6 g	NaHSO ₃ -compound,
348,0 g	Reaction product of an unsaturated fatty acid (having 65 wt.% of conjugated linoleic acid) and propylene oxide (acid number<1, Mw = 348), and
100,0 g	o-xylene.

The mixture was heated to about 130°C, with the solvent present being distilled off under reduced pressure. After cooling to about 50°C a mixture of

222 g of isophorone diisocyanate and 70 g of methylethyl ketone was added to the reaction mixture, after which the reaction mixture was kept at 120°C for 2 hours. Dibutyl tin diacetate (5 or 6 drops) was added and the reaction was maintained at 120°C for 3 hours. 1-Methoxypropanol-2 (265,3 g) was added
5 and the reactor contents were cooled to ambient temperature. The prepared unsaturated polyurethane had a solids content of about 75 wt.%.

Preparation of Unsaturated Polyurethane B

10 The following compounds were weighed into a 2 l reaction flask:
194,7 g Tegomer[®] D-3123,
344,6 g NaHSO₃-compound,
541,0 g Reaction product of an unsaturated fatty acid (having 65 wt.% of
conjugated linoleic acid) and Cardura[®] E 10 (acid number < 1,
15 Mw = 541), and
100,0 g o-xylene.

Unsaturated Polyurethane B was prepared following the procedure for the preparation of Unsaturated Polyurethane A, except that 83,5 g of methylethyl
20 ketone were added to the reaction mixture and on completion of the reaction as above the reactor contents were diluted with 316,3 g of 1-methoxypropanol-2. The prepared unsaturated polyurethane had a solids content of about 75 wt.%.

25

Preparation of Unsaturated Polyurethane C

The following compounds were weighed into a 2 l reaction flask:

- 194,7 g Tegomer[®] D-3403,
344,6 g NaHSO₃-compound,
348,0 g Reaction product of an unsaturated fatty acid (having 65 wt.% of
conjugated linoleic acid) and propylene oxide (acid number<1,
5 Mw = 348), and
100,0 g o-xylene.

Unsaturated Polyurethane C was prepared following the procedure for the
preparation of Unsaturated Polyurethane A, except that 70 g of methylethyl
10 ketone were added to the reaction mixture and on completion of the reaction
as above the reactor contents were diluted with 265,3 g of 1-methoxypropanol-
2. The prepared unsaturated polyurethane had a solids content of about 75
wt.%.

15 Preparation of Unsaturated Polyurethane D

The following compounds were weighed into a 2 l reaction flask:

- 194,7 g Tegomer[®] D-3403,
344,6 g NaHSO₃-compound,
20 267,0 g Oleyl/linoleyl alcohol (available from Henkel under the trade
designation HD-Ocenol 110/130), and
100,0 g o-xylene.

Unsaturated Polyurethane D was prepared following the procedure for the
25 preparation of Unsaturated Polyurethane A, except that 64,3 g of methylethyl
ketone were added to the reaction mixture and on completion of the reaction
as above the reactor contents were diluted with 244 g of 1-methoxypropanol-2.
The prepared unsaturated polyurethane had a solids content of about 75 wt.%.

Preparation of Unsaturated Polyurethane E

The preparation of Unsaturated Polyurethane D was repeated, except that oleyl alcohol (available from Henkel under the trade designation HD-Ocenol® 90/95) was employed instead of HD-Ocenol 110/130.

Preparation of Unsaturated Polyurethane F

The following compounds were weighed into a 2 l reaction flask:

10	118,0 g	Tegomer® D-3403,
	411,5 g	NaHSO ₃ -compound,
	267,0 g	Oleyl alcohol (available from Henkel under the trade designation HD-Ocenol® 90/95), and
	100,0 g	o-xylene.

15

Unsaturated Polyurethane F was prepared following the procedure for the preparation of Unsaturated Polyurethane A, except that 62,2 g of methylethyl ketone were added to the reaction mixture and on completion of the reaction as above the reactor contents were diluted with 236 g of 1-methoxypropanol-2.

20 The prepared unsaturated polyurethane had a solids content of about 75 wt. %.

Preparation of Unsaturated Polyurethane G

25 The following compounds were weighed into a 2 l reaction flask:

	265,5 g	Tegomer® D-3403,
	282,9 g	NaHSO ₃ -compound,
	267,0 g	oleyl alcohol (available from Henkel under the trade designation HD-Ocenol® 90/95), and

100,0 g o-xylene.

Unsaturated Polyurethane G was prepared following the procedure for the preparation of Unsaturated Polyurethane A, except that 66,2 g of methylethyl ketone were added to the reaction mixture and on completion of the reaction
5 as above the reactor contents were diluted with 251,3 g of 1-methoxypropanol-2. The prepared unsaturated polyurethane had a solids content of about 75 wt.%.
10

Preparation of Unsaturated Polyurethane H

The following compounds were weighed into a 2 l reaction flask:

194,7 g Tegomer[®] D-3403,
334,6 g NaHSO₃-compound,
15 133,5 g Oleyl alcohol (HD Ocenol[®] 90/95),
500,0 g Polypropylene glycol (Mw = 2000), and
100,0 g o-xylene.

Unsaturated Polyurethane H was prepared following the procedure for the preparation of Unsaturated Polyurethane A, except that 66,2 g of methylethyl ketone were added to the reaction mixture and on completion of the reaction
20 as above the reactor contents were diluted with 251,3 g of 1-methoxypropanol-2. The prepared unsaturated polyurethane had a solids content of about 75 wt.%.
25

Unsaturated Polyurethane I

Unsaturated Polyurethane I was prepared from 0.33 molequivalents Tegomer[®] D-3403, 0.67 molequivalents of NaHSO₃-compound, 2 molequivalents of

oleylalcohol (HD Ocenol[®] 90/95), and 2 molequivalents isophorone diisocyanate. LiOH. H₂O was added until pH=7.

Unsaturated Polyurethane J

5

Unsaturated Polyurethane J was prepared from 0.33 molequivalents Tegomer[®] D-3403, 0.67 molequivalents of NaHSO₃-compound, 1 molequivalents of oleylalcohol (HD Ocenol[®] 90/95), 1 molequivalents of polypropylene glycol 600, and 2,5 molequivalents isophorone diisocyanate.

10 LiOH. H₂O was added until pH=7.

Preparation of Aqueous Alkyd Dispersion

The following alkyd resins were employed:

15

Alkyd Resin A

Alkyd resin having an oil length of 55, acid number = 8,3 mg KOH/g, Mn = 3230, Mw = 71 160 dissolved in 1-methoxypropanol-2, and a solids content of

20 75 wt.%.

Alkyd Resin B

Alkyd resin having an oil length of 65, acid number = 6,9 mg KOH/g, Mn = 3650, Mw = 47 980 dissolved in 1-methoxypropanol-2, and a solids content of

25 80 wt.%.

Preparation of Aqueous Alkyd Dispersions

Example 1

Into a 2 l reaction flask were weighed:

- | | |
|--------------|--|
| 550 g | Alkyd Resin A (75 wt.% in 1-methoxypropanol-2) and |
| 5 116,7 g | Unsaturated Polyurethane A (75 wt.% in a mixture of methylethyl ketone and 1-methoxypropanol-2). |

The mixture was heated to 130°C. All solvents were distilled off under reduced pressure. The mixture was cooled to about 90°C, and demineralised water
10 was added slowly with vigorous stirring. In all, 550 g demineralised water were added over 3 hours, with the temperature gradually being lowered to ambient. Obtained was a stable aqueous alkyd dispersion having the properties listed in Table 1.

15 Example 2

Example 1 was repeated, except that prior to the distilling off of the solvents 1,75 g of LiOH.H₂O (= 2 wt.%, calculated on the solid unsaturated polyurethane) were added to the mixture of alkyd resin and unsaturated
20 polyurethane. Obtained was a stable aqueous alkyd dispersion with the properties listed in Table 1. Compared with example 1, the alkyd dispersion of example 2 has a smaller particle size and a higher pH.

Examples 3 through 8

25

Example 2 was repeated, except that use was made of ever decreasing amounts of unsaturated polyurethane. The amounts employed and the properties of the resulting alkyd dispersions are listed in Table 1. Although there was an increase in the average particle size of the alkyd dispersions in

examples 3-8, stable dispersions were obtained in all cases. There was an increase in solids contents from 50 to 62, while the average particle size increased from 164 to 527 nm.

5 Examples 9 through 12

Example 2 was repeated, except that Alkyd Resin B was employed instead of Alkyd Resin A and Unsaturated Polyurethane B was used instead of Unsaturated Polyurethane A, the alkyd resin/polyurethane dispersing resin
10 ratio being 85/15 (solids to solids) in all cases, with an increasing percentage of LiOH.H₂O (calculated on the unsaturated polyurethane) in examples 9-12. In all cases stable alkyd dispersions in water were obtained, with properties as listed in Table 2.

15

20

Example 13

Weighed into a 2 l reaction flask were:

590,0 g	Alkyd Resin A (75 wt.% in 1-methoxypropanol-2),
25 76,7 g	Unsaturated Polyurethane C (75 wt.% in a mixture of methylethyl ketone and 1-methoxypropanol-2), and
1,064 g	LiOH.H ₂ O .

The mixture was heated to 130°C. All solvents were distilled off under reduced pressure. The mixture was cooled to about 90°C and demineralised water was added slowly with vigorous stirring. In all, 365 g demineralised water were added over a period of 3 hours, with the temperature gradually being lowered to ambient. Obtained was a stable aqueous alkyd dispersion having the properties listed in Table 3.

Examples 14 through 17

Example 13 was repeated, except that use was made of Unsaturated Polyurethanes D through G instead of Unsaturated Polyurethane C. Obtained were stable aqueous alkyd dispersions having properties as listed in Table 3.

15

20 Example 18

Weighed into a 2 l reaction flask were:

680,0 g	Alkyd Resin A (75 wt.% in 1-methoxypropanol-2),
120,0 g	Unsaturated Polyurethane H (75 wt.% in a mixture of methylethyl ketone and 1-methoxypropanol-2), and
1,44 g	LiOH.H ₂ O.

The mixture was heated to 130°C. All solvents were distilled off under reduced pressure. The mixture was cooled to about 90°C and demineralised water was

added slowly with vigorous stirring. In all, 438,5 g demineralised water were added over a period of 3 hours, with the temperature gradually being lowered to ambient. Obtained was a stable aqueous alkyd dispersion having the properties listed in Table 3.

5

Example 19

Example 14 was repeated, except that after removal of the solvent there were added to the mixture of alkyd and unsaturated polyurethane 2,175 g of
10 Cobalt(II)acetyl acetonate and 2,25 g of methylethyl ketoxim (anti-skinning agent). Obtained was a stable aqueous alkyd dispersion having the properties listed in Table 4.

Example 20

15

Example 14 was repeated, except that after removal of the solvent there were added to the mixture of alkyd resin and unsaturated polyurethane 2,175 g of Cobalt(II)acetyl acetonate, 1,8 g of Zr(IV)acetyl acetonate, and 2,25 g of methylethyl ketoxim (anti-skinning agent). Obtained was a stable aqueous
20 alkyd dispersion having the properties listed in Table 4.

Example 21

25

Solvent was removed from a mixture of 640 g Alkyd Resin A and 160 g Unsaturated Polyurethane D by distillation under reduced pressure at 130°C. After removal of solvent the mixture was cooled to 80°C. In a period of 30 minutes 500 g of this mixture were pumped into a 2 l reactor which was

equipped with a stirrer and baffles and filled with 600 g demineralised water in which 2,5 g of $\text{LiOH} \cdot \text{H}_2\text{O}$ had been dissolved. There was vigorous stirring during this process. Obtained was a stable aqueous alkyd dispersion with $\text{pH}=8.5$, an average particle size of 135 nm, and a polydispersity of 0.03.

5

Pigmented aqueous alkyd dispersions

Example 22

10 Weighed into a 2 l reaction flask were:

500,0 g pigment paste composed of 68 wt.% TiO_2 , 12,6 wt.% Alkyd Resin B, and 19,4 wt.% white spirit,

417,5 g Alkyd Resin A (75 wt.% in 1-methoxypropanol-2),

65,2 g Unsaturated Polyurethane A (75 wt.% in a mixture of 1-methoxypropanol-2 and methylethylketone) and

15

1,44 g $\text{LiOH} \cdot \text{H}_2\text{O}$.

The mixture was heated to 150°C . All solvents were distilled off under reduced pressure. The mixture was cooled to about 90°C , and demineralised water
20 was added slowly with vigorous stirring. In all, 328 g demineralised water were added over a period of 3 hours, with the temperature gradually being lowered to ambient. Obtained was a stable, pigmented aqueous alkyd dispersion having the properties listed in Table 5.

25 Example 23

Example 22 was repeated, except that the following constituents and amounts were employed:

- 500,0 g pigment paste composed of 68 wt.% TiO₂, 12,6 wt.% Alkyd Resin B, and 19,4 wt.% white spirit,
- 397,6 g Alkyd Resin A (75 wt.% in 1-methoxypropanol-2),
- 85,0 g Unsaturated Polyurethane B (75 wt.% in a mixture of 1-methoxypropanol-2 and methylethylketone) and
- 5 1,05 g LiOH.H₂O .

360 g demineralised water were added. Obtained was a stable, pigmented aqueous alkyd dispersion having the properties listed in Table 5.

10

Example 24

Example 22 was repeated, except that the following constituents and amounts were employed:

- 15 500,0 g pigment paste composed of 68 wt.% TiO₂, 12,6 wt.% Alkyd Resin B, and 19,4 wt.% white spirit,
- 397,6 g Alkyd Resin A (75 wt.% in 1-methoxypropanol-2),
- 8,0 g Unsaturated Polyurethane B (75 wt.% in a mixture of 1-methoxypropanol-2 and methylethylketone), and
- 20 1,05 g LiOH.H₂O .

After the solvent had been distilled off there were added:

- 7,1 g Sologen® Cobalt Aqua (containing 6 wt.% of Co),
- 1,9 g methylethyl ketoxim (anti-skinning agent), and
- 344 g demineralised water.
- 25 Obtained was a stable pigmented aqueous alkyd dispersion having the properties listed in Table 5.

Unsaturated polyurethanes as Pigment Dispersants

Example 25

Into a 2 l flask were weighed 400,0 g Unsaturated Polyurethane A (75 wt.% in a mixture of 1-methoxypropanol-2 and methylethylketone) and 0,45 g
5 LiOH.H₂O. The mixture was heated to 130°C, and all solvents were distilled off under reduced pressure. The mixture was cooled to about 90°C, and 670 g demineralised water were added over a period of 3 hours with vigorous stirring of the contents of the reaction flask while the temperature was gradually
10 lowered to ambient. Obtained was a colloidal dispersion having the properties listed in Table 6.

Example 26

Example 25 was repeated, except that use was made of 400,0 g Unsaturated
15 Polyurethane C (75 wt.% in a mixture of 1-methoxypropanol-2 and methylethylketone) and 0,3 g LiOH.H₂O. After the solvents had been distilled off, 700 g demineralised water were added. Obtained was a colloidal dispersion having the properties listed in Table 6.

20 Example 27

Example 26 was repeated, except that use was made of 400 g Unsaturated Polyurethane D (75 wt.% in a mixture of 1-methoxypropanol-2 and methylethylketone) and 0,225 LiOH.H₂O. Obtained was a colloidal dispersion
25 having the properties listed in Table 6.

Example 28

Example 27 was repeated, except that use was made of 400 g Unsaturated Polyurethane H (75 wt.% in a mixture of 1-methoxypropanol-2 and methylethylketone) and 0,18 g LiOH.H₂O. Obtained was a colloidal dispersion having the properties listed in Table 6.

5

The aqueous unsaturated polyurethanes according to the invention are also readily usable as pigment (in these examples, TiO₂) dispersing agents. Stable pigment pastes were obtained using unsaturated polyurethanes of examples 25-28. In these examples, about 1-10 wt.% (on solids) unsaturated

10

polyurethanes are used in relation to TiO₂.

15

Composite Latexes (Composite Polymer Dispersions)

Example 29

20

In a 2 l reaction flask equipped with a stirrer, a thermometer, a reflux condenser, and two dropping funnels a mixture composed of 520,8 g alkyd dispersion from Example 15 (57,6 wt.% of solids) and 222,8 g demineralised water was homogenised.

25

The first Dropping Funnel A was filled with a pre-emulsion composed of:

0,8 g	sodium dodecyl benzene sulphonic acid,
69,9 g	demineralised water,
50,0 g	methyl methacrylate, and

150,0 g butyl methacrylate.

The second Dropping Funnel B was filled with a homogeneous mixture of:

1 g sodium persulphate and
5 100 g demineralised water.

After deaeration the reaction flask and the dropping funnels were placed under a nitrogen atmosphere. The contents of the reaction flask were heated to 85°C, after which the contents of Dropping Funnel A and 95% of the contents
10 of Dropping Funnel B were added to the reaction flask over a period of 1,5 hours, with the temperature of the contents of the reaction flask being kept at 85°C. After the contents of the reaction flask had been kept at 85°C for one hour, the remaining contents of Dropping Funnel B were added to the reaction
15 flask, which was then kept at 85°C for an additional hour. The contents were cooled to ambient temperature, and the composite latex was filtered to remove a slight amount of coagulation. The properties of the obtained composite latex are listed in Table 7.

Example 30

20

In a 2 l reaction flask equipped with a stirrer, a thermometer, a reflux condenser, and two dropping funnels a mixture composed of

434,0 g Alkyd dispersion from Example 15 (57,6 wt.% of solids) and
217,6 g demineralised water.

25 was homogenised.

The first Dropping Funnel A was filled with a pre-emulsion composed of:

1 g sodium dodecyl benzene sulphonic acid,
87,3 g demineralised water,

62,5 g methyl methacrylate, and
187,5 g butyl methacrylate.

The second Dropping Funnel B was filled with a homogeneous mixture of:

5 1,25 g sodium persulphate and
125 g demineralised water.

After deaeration the reaction flask and the dropping funnels were placed under a nitrogen atmosphere. The contents of the reaction flask were heated to
10 85°C, after which the contents of Dropping Funnel A and 95% of the contents of Dropping Funnel B were added to the reaction flask over a period of 2 hours, with the temperature of the contents of the reaction flask being kept at 85°C. After the contents of the reaction flask had been kept at 85°C for one hour, the remaining contents of Dropping Funnel B were added to the reaction
15 flask, which was then kept at 85°C for an additional hour. The contents were cooled to ambient temperature, and the composite latex was filtered to remove a slight amount of coagulation. The properties of the obtained composite latex are listed in Table 7.

20 Unsaturated polyurethanes as pigment dispersants in pigmented aqueous alkyd dispersions

Examples 31-33

25 A pigment paste A was prepared from 35 g water, 2,4 g nonionic and anionic dispersant, i.e. Atsurf ex ICI, 4,5 g wetting agent, i.e. Surfynol TG ex Air Products, 106 g TiO₂, 0,36 defoamer, i.e. Byk 24, and 1,85 g of a heur thickener, i.e. RM 2020, ex. Rohm & Haas.

A pigment paste B was prepared from 26 g water, 13,5 Unsaturated Polyurethane J, 4,5 g wetting agent, i.e. Surfynol TG ex Air Products,, 106 g TiO₂, and 0,36 defoamer, i.e. Byk 24.

- 5 Both pigment pastes A and B were used to prepare pigmented aqueous alkyd dispersions. A 150 μ layer was applied with the pigmented aqueous coating compositions. The gloss of the wet paint was measured. The König hardness was measured after several drying periods. The drying velocity of the applied coating composition at 10°C was followed directly after preparation of the
- 10 coating composition and after an aging period of 4 weeks at 35°C of the coating composition. The compounds and amounts used and the resulting properties of the dispersions and coating compositions are listed in Table 8.

Table 1
Aqueous alkyd dispersions

Composition	Examples							
	1	2	3	4	5	6	7	8
Alkyd Resin A (wt.%)	82,5	82,5	83,5	87,5	89,5	91,5	92,5	93,5
UP A (wt.%) ¹	17,5	17,5	16,5	12,5	10,5	8,5	7,5	6,5
LiOH.H ₂ O (wt.%) (calc. on UP A)	-	2,0	1,75	1,8	1,9	2,1	2,25	2,45
Properties								
wt.% solids	49,6	46,6	49,9	55,1	58,0	60,2	61,2	62,3
viscosity (Pa.s)	0,44	0,12	0,32	0,30	0,32	0,23	0,30	0,24
pH	4,1	8,7	8,15	7,7	7,9	7,6	7,9	7,9
particle size (nm)	293	148	164	215	263	320	373	527
polydispersity	0,05	0,03	0,01	0,05	0,01	0,15	0,09	0,03

5 ¹ UP=Unsaturated Polyurethane

Table 2

Aqueous alkyd dispersions

5

Composition	Examples			
	9	10	11	12
Alkyd Resin B (wt. %)	85	85	85	85
Unsaturated Polyurethane B (wt. %)	15	15	15	15
LiOH.H ₂ O (wt. %) (calc. on UP ¹ B)	1,5	2,0	2,6	3,0
Properties				
wt. % solids	60,9	58,0	53,9	50,9
viscosity (Pa.s)	0,23	0,19	0,21	0,17
pH	6,5	6,75	7,6	7,8
particle size (nm)	~3000	740	256	236
polydispersity	-	0,08	0,03	0,08

¹ UP=Unsaturated Polyurethane

10

Table 3

Aqueous alkyd dispersions

Composition	Examples					
	13	14	15	16	17	18
Alkyd Resin A (wt. %)	88,5	88,5	88,5	88,5	88,5	88,5
Unsaturated Polyurethane	C	D	E	F	G	H
wt. % Unsaturated Polyurethane	11,5	11,5	11,5	11,5	11,5	15,0
LiOH.H ₂ O (wt. %) (calc. on UP ¹)	1,85	1,85	1,85	1,85	1,85	1,60
Properties						
wt. % solids	57,8	57,8	57,6	57,7	57,7	57,8
viscosity (Pa.s)	0,46	0,45	0,38	0,51	0,37	0,41
pH	7,8	7,8	8,0	8,0	8,0	8,0
particle size (nm)	222	215	236	234	235	225
polydispersity	0,01	0,02	0,01	0,04	0,03	0,07

5 ¹ UP=Unsaturated Polyurethane

Table 4

Aqueous alkyd dispersions

5

Composition	Examples	
	19	20
Alkyd Resin A (wt.%)	88,5	88,5
Unsaturated Polyurethane D (wt.%)	11,5	11,5
LiOH.H ₂ O (wt.%) (calc. on UP ¹ D)	1,85	1,85
Co(II)Ac.Ac.	0,435	0,435
Zr(IV)Ac.Ac.	-	0,360
anti-skinning agent	0,45	0,45
Properties		
wt. % solids	57,6	56,4
viscosity (Pa.s)	0,29	0,21
pH	7,9	7,8
particle size (nm)	236	221
polydispersity	0,03	0,03

¹ UP=Unsaturated Polyurethane

Table 5

Pigmented aqueous alkyd dispersions

5

Properties	Examples		
	22	23	24
wt. % solids	70,0	67,0	67,8
viscosity (Pa.s)	0,61	0,37	0,50
pH	7,6	7,8	7,2
particle size (nm) ¹	540	610	510

¹ Malvern, small angle light scattering

Table 6

10

Pigment unsaturated polyurethanes

Properties	Examples			
	25	26	27	28
wt. % solids	30,9	29,8	29,9	29,8
viscosity (Pa.s)	1,90	0,82	0,91	0,82
pH	7,9	7,6	7,4	7,0

Table 7

Composite latexes

5

Properties	Examples	
	29	30
wt.% solids	44,8	44,6
viscosity (Pa.s)	0,03	0,04
pH	6,9	6,5
particle size (nm)	207	208
polydispersity	0,04	0,10

Table 8

Composition	Examples		
	31	32	33
Alkyd Resin A (88,5 wt. %)+ UP ¹ I (11,5 wt%)	56 g	48 g	50 g
water	3,8 g	16 g	11,3 g
Co siccativ: ASK 2005, ex. Ashland	1 g	0,9 g	0,9 g
methylethylketoxim	0,5 g	0,5 g	0,5 g
Pigment Paste A	35,9 g		32 g
Pigment Paste B		32,8 g	
RM 2020, ex. Rohm & Haas	2,8 g	6 g	5 g
Dispersion properties			
wt. % solids	47	41	41
ICI viscosity	3	3	3
pH	7,1	7	7,1
Paint properties			
Gloss (20°C, after 1 day)	84	87	83
König Hardness (1 day, 1 week, 100 hrs/50°C)	6/8/25	8/9/25	9/16/27
Drying (10 °C)	ok	ok	ok
Drying (10°C after aging for 4 weeks/35°C)	ok	ok	ok

¹ UP=Unsaturated Polyurethane

Claims

1. A water-dispersible unsaturated polyurethane comprising pendant
5 unsaturated alkyl groups, pendant sulphonic acid salt groups, and
polyoxyalkylene groups, said sulphonic acid salt groups and said
polyoxyalkylene groups being present in amounts at least sufficient to
render said unsaturated polyurethane water dispersible, characterised
10 in that the polyoxyalkylene groups are pendant alkoxy polyoxyalkylene
groups.
2. An unsaturated polyurethane according to claim 1, characterised in that
the alkoxy polyoxyalkylene groups are C1-C4 alkoxy polyoxyalkylene
15 groups.
3. An unsaturated polyurethane according to claim 2, characterised in that
the alkoxy polyoxyalkylene group is a methoxypolyoxyethylene group, a
methoxypolyoxypropylene group, or a combination thereof.
- 20 4. An unsaturated polyurethane according to any one of the preceding
claims, characterised in that the alkoxy polyoxyalkylene group has an
average molecular weight of 500-3000.
- 25 5. An unsaturated polyurethane according to any one of the preceding
claims, characterised in that said unsaturated polyurethane comprises:
 - a) 10-40 wt.% alkoxy polyoxyalkylene groups,
 - b) 0,1-0,5 meq/g sulphonic acid alkali metal salt groups, and
 - c) 10-35 wt.% unsaturated alkyl groups.

6. An unsaturated polyurethane according to any one of the preceding claims, characterised in that said unsaturated polyurethane comprises a chain extender group.
- 5 7. An unsaturated polyurethane according to claim 6, characterised in that said chain extender group is derived from a polyester diol or polyether diol.
- 10 8. An unsaturated polyurethane according to any one of the preceding claims, characterised in that one or more of the unsaturated alkyl groups are polyunsaturated.
- 15 9. An unsaturated polyurethane according to any one of the preceding claims, characterised in that the sulphonic acid salt groups are derived from a sulphosuccinate diester diol.
- 20 10. An unsaturated polyurethane according to any one of the preceding claims, characterised in that the unsaturated alkyl groups are derived from a compound which is a reaction product of an unsaturated fatty acid and mono-epoxide.
- 25 11. An unsaturated polyurethane according to any one of the preceding claims, characterised in that the unsaturated polyurethane further comprises a compound derived from a isocyanate-functional compound.
12. An aqueous alkyd dispersion comprising an unsaturated polyurethane according to any one of the preceding claims.

13. An aqueous alkyd dispersion according to claim 12, characterised in that the alkyd resin is wholly or partially neutralised with alkali metal hydroxide.
- 5 14. An aqueous alkyd dispersion according to any of the preceding claims 12 and 13, characterised in that said dispersion comprises 5-25 wt.% unsaturated polyurethane and 95 to 75 wt.% alkyd resin.
- 10 15. An aqueous alkyd dispersion according to any one of claims 12 to 14, characterised in that the alkyd resin has an oil length of 40-90 and an acid number of 5-10 mg KOH/g.
- 15 16. A process for preparing a polymer dispersion, characterised in that monoethylenically unsaturated monomers are reacted in the presence of an alkyd dispersion according to any one of the preceding claims 12 to 15.
- 20 17. A process according to claim 16, characterised in that the monoethylenically unsaturated monomers are alkyl (meth)acrylate compounds.
- 25 18. A process according to claim 17, characterised in that the alkyl (meth)acrylate is selected from the group of methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, or isobutyl (meth)acrylate and mixtures thereof.
19. Use of an unsaturated polyurethane according to any one of the preceding claims 1-11 for emulsifying an alkyd resin in water.

20. Use of an unsaturated polyurethane according to any one of the preceding claims 1-11 for dispersing pigments in water.
21. Use of an unsaturated polyurethane according to any one of the preceding claims 1-11 in a pigmented coating composition comprising an alkyd resin and a pigment or pigment paste.
22. Use of a polymer dispersion prepared according to any one of the preceding claims 16-18 in a pigmented coating composition comprising a pigment or pigment paste.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 96/05156

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G18/08 C08G18/46 C08G18/48 C08G18/40 C08F290/14
 C08F283/00 C09D17/00 C09D7/02 C08J3/03 //C08L67:08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 501 852 A (MARKUSCH PETER H ET AL) 26 February 1985 see claims 1-6,11 see column 5, line 53 - column 6, line 18 see column 7, line 11 - column 8, line 23 ---	1
A	US 4 150 946 A (NEEL JEAN ET AL) 24 April 1979 see claims 1-8,17,35-42 see column 2, line 60 - line 65 -----	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 March 1997

Date of mailing of the international search report

12. 03. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+ 31-70) 340-3016

Authorized officer

Van Puymbroeck, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/05156

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4501852 A	26-02-85	CA 1249391 A	24-01-89
		DE 3468426 A	11-02-88
		EP 0148970 A	24-07-85
		JP 1712542 C	27-11-92
		JP 4000488 B	07-01-92
		JP 60004515 A	11-01-85

US 4150946 A	24-04-79	NONE	
